Chapter 2: Infiltration and Distribution of Ethanol and Ethanol-blended Gasoline in the Vadose Zone

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Table of Contents

List of Tables

List of Figures

Summary
(Infiltration and Distribution of Ethanol and
Ethanol-blended Gasoline in the Vadose Zone)

We have very little information on the behavior of ethanol-containing gasoline as it infiltrates through the unsaturated zone. To better understand these unsaturated zone processes, additional research was conducted. The research presented in this chapter found that the addition of ethanol to gasoline changes the nature of the capillary phenomena affecting gasoline infiltration and distribution at the water table due to the extensive and rapid partitioning of ethanol in to soil moisture and the associated reduction in the interfacial and surface tension between the phases. These changes affect the environmental behavior of gasoline containing ethanol in the following ways:

- There is less residual gasoline entrapped in the unsaturated zone following the spill of ethanol-blended gasoline compared with a standard gasoline. The reduced surface and interfacial tension in the presence of ethanol ultimately results in more complete drainage of fluids from the region.

- A significant fraction of ethanol partitions into, and is retained by, the residual water in the unsaturated zone during gasoline infiltration. Depending on the volume of the spill, this ethanol could then drain slowly into the gasoline pool, creating a central region with high ethanol concentration. The remainder of the pool appears much the same as a spill of gasoline without ethanol.

- The fraction of ethanol retained in the unsaturated zone depends greatly on the volume of soil involved, the water content, and the rate that gasoline enters the subsurface. The rate that the ethanol-laden water in the unsaturated zone drains to the capillary fringe is limited by the increased viscosity and, therefore, reduced unsaturated hydraulic conductivity of this phase. Functional relationships to describe these processes have not yet been developed.

Bulk ethanol releases at distribution terminals can affect the behavior of previously released fuel hydrocarbons in the following ways:

- Bulk ethanol dissolves and mobilizes light nonaqueous phase liquid (LNAPL) entrapped in the unsaturated and saturated zones. This process creates regions in the vadose zone with high saturation that can drain towards the capillary fringe. The net result is a substantial decrease in the LNAPL entrapped in the unsaturated zone.

- Ethanol creates a capillary fringe depression into which all nearby LNAPL can drain. The reduction in surface tension, and, therefore, the height of the capillary fringe in the region that ethanol infiltrates, essentially creates a depression into which all nearby LNAPL can drain. The LNAPL in this region has a reduced interfacial tension, allowing it to fill a greater fraction of the pore spaces. The net result is a region with high LNAPL saturation that would be very mobile.

- The wetting properties of soils could change as the result of a bulk ethanol spill. At a bulk ethanol release site with fuel hydrocarbons present, it appears that significant surfactant concentrations, which affect capillary properties, exist in the aqueous phase. It is possible that their presence could be related to the stimulation of the microbial community in the presence of ethanol. Additional research would be required to confirm these mechanisms.

The results of research presented in this chapter suggest that there is still significant uncertainty in the magnitude of the effects examined. For a ethanol-blended gasoline spill, uncertainty in the amount of ethanol that is retained in the unsaturated zone prevents us from adequately predicting the composition of gasoline that accumulates in a pool at the capillary fringe and, therefore, the flux of contaminants from the source area into groundwater. Additional research is needed at several levels to provide sufficient information to predict ethanol and BTEX fluxes to groundwater. The specific vadose zone studies that are recommended include:

- Laboratory studies to better quantify the functional relationships that control the retention of ethanol in the unsaturated zone. These studies should examine the retention of ethanol as a function of soil type, moisture content and spill rate, and should include laboratory tests to better define the significance of the observed reversal from water wetting to LNAPL wetting.

- Numerical modeling. Improved modeling efforts are needed to better represent the complex behavior of gasoline LNAPL in the presence of ethanol. A spill of ethanol-blended gasoline into the subsurface should not be modeled as a pool of gasoline with constant composition throughout. This modeling should include the partitioning of ethanol into the aqueous phase of the unsaturated zone as well as the resulting change in interfacial properties, flow characteristics, and cosolvency.

- A field-scale test that includes the release of ethanol blended gasoline under unsaturated conditions. A field-scale controlled release is needed to validate in the field processes observed in the laboratory and to calibrate predictive models of the long-term net flux of ethanol and BTEX into groundwater.

Although mostly qualitative, the results of this investigation also provide a basis for recommendations regarding the remediation of soil contaminated with ethanol or ethanol-blended gasoline:

- Increased mobility can enhance LNAPL recovery. Because the spill of ethanol into soil previously contaminated by an LNAPL consolidates the LNAPL into a pool with high mobility, an opportunity exists for effective free-phase recovery of the LNAPL that would have not have otherwise been available. Efforts to recover this LNAPL should be made in a timely fashion.

- Enhanced bioremediation within the unsaturated zone. The retention of ethanol in the unsaturated zone after the spill of ethanol-blended gasoline could provide an opportunity for biodegradation of the ethanol prior to its entry into the saturated groundwater zone. Oxygen, which is likely to become limited, should be added to the unsaturated zone in some form to enhance the rate of ethanol degradation in this region.

2. Infiltration and Distribution of Ethanol and Ethanol-blended Gasoline in the Vadose Zone

2.1. Introduction

As discussed in Chapter 1, the results of the California health and environmental assessment of the use of ethanol as a fuel oxygenate (Rice *et al.*, 1999b) identified several important gaps in our knowledge about the fate of ethanol in the environment and its impacts on other gasoline constituents. The migration and distribution of ethanol-blended gasoline in the subsurface unsaturated zone is one of the areas identified as a knowledge gap. The initial phenomena that affect the manner in which gasoline enters the ground could substantially alter the flux of contaminants from the gasoline to groundwater. Thus, our insufficient current understanding of these processes will limit our ability to adequately predict the extent of groundwater contamination and human health risk due to the presence of ethanol in gasoline.

The goal of the report presented here is to provide additional knowledge so that we can better understand the infiltration and migration processes as gasoline enters the subsurface that could be affected by the presence of ethanol. Understanding this initial process that controls the distribution of gasoline in the subsurface is necessary for subsequent estimates of the net flux of contaminants from the gasoline to groundwater. This report provides a review of pertinent literature in this area as well as results of experiments conducted specifically for this purpose.

Although there is currently a paucity of data from leaking UST sites, there have been documented sites involving the release of denatured ethanol from an above ground storage tank at a bulk terminal. One such spill occurred at a site in the Pacific Northwest (PNW) in 1999 (Buscheck *et al.*, 2001a). A significant amount of data has been collected from this site, including several rounds of sampling that included NAPL thickness, GW elevations, and groundwater concentrations. As described on the following page, changes in the NAPL thickness at this site have raised additional questions about the potential for ethanol to alter hydrocarbon infiltration mechanisms and distribution in the unsaturated zone and at the capillary fringe.

2.2. Overview of the Fate of Ethanol-blended Gasoline in the Subsurface

The presence of oxygenate chemicals in gasoline can potentially impact their migration and fate in the subsurface following a spill or leak. In general, public health concerns with gasoline in the subsurface arise from the presence of dissolved species in groundwater that could be used for drinking purposes. Numerous processes affect the concentration of such chemicals in aquifers. Generally, these processes include the infiltration of the gasoline through the unsaturated zone of the subsurface, spreading of the gasoline pool at the water table, dissolution of slightly soluble species from the gasoline into the water, transport of these chemicals with the

Denatured ethanol spill at a bulk petroleum storage terminal

The Pacific Northwest Terminal (PNW site) began petroleum-processing operations in 1911, distributing and blending a variety of refined petroleum products, including gasoline, diesel, stove oil, turbine oil, transmission fluid and lubrication oils. Two other terminals located to the southeast and northwest border the Pacific Northwest Terminal.

In March 1999, a 19,000-gallon release of neat ethanol occurred from an above ground storage tank (#58) at this site. Historical groundwater monitoring data were available from existing monitoring wells to delineate a pre-existing dissolved hydrocarbon plume. Eighteen new monitoring wells were installed over an 18-month period in response to the March 1999 ethanol release. The presence of ethanol has affected pre-existing petroleum hydrocarbon in both the NAPL and the dissolved phases. NAPL thickness in a near-source monitoring well has been quite variable since the spill, exceeding two feet at times. Wells CR-10, CR15 and CR-19 all have deeper LNAPL pools since the ethanol spill. In one downgradient well (CR-7), benzene concentrations increased by a factor of 15 five months after the release and have since remained about ten times above the pre-release level, suggesting evidence for cosolvent effects of ethanol and lower benzene intrinsic biodegradation rates.

The subsurface at this site consists of a 0-30 ft. layer of fill, overlaying alluvium to a depth of approximately 50 ft., with basaltic materials at greater depths. The fill is very loose to medium dense and fine to medium grained sand and silty sand. Both the water table (2-14 ft. below grade) and the hydrocarbon contamination exist predominantly in the fill layer. Groundwater moves from the site towards a river that is located approximately 1500 feet to the east. Water levels beneath the site are influenced by annual precipitation cycles and by river stage fluctuations.
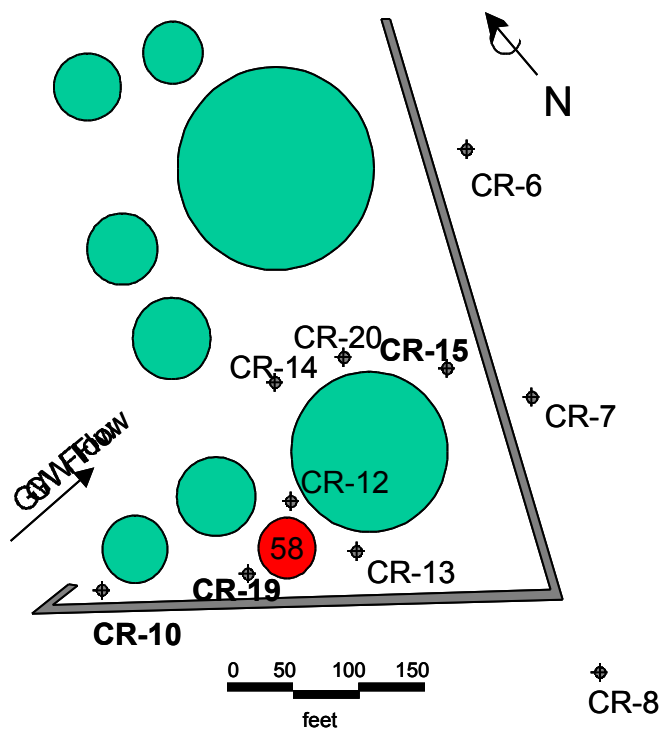
(Note – this summary is adapted from Buscheck *et al.*, 2001b)

groundwater towards a potential point of contact such as a groundwater well and loses such as sorption or biodegradation (Figure 2-1). Differences in the biodegradability and hydrophobicity of ethanol relative to standard gasoline components contribute to the impact of ethanol on the overall fate of BTEX species in groundwater (Powers *et al*., 2001).

2.3. Mechanisms that Affect the Fate of Gasohol During Infiltration and Spreading

Gasoline from a leak or spill infiltrates through the unsaturated zone of the subsurface predominantly under gravitational forces. A fraction of the gasoline is retained in the pore spaces due to interfacial forces, creating a residual saturation of gasoline that generally occupies 1–7% of the pore space in the unsaturated zone. Gasoline that migrates to the top of the capillary fringe begins to spread horizontally as it floats on the water. Some gasoline will also continue to migrate vertically and laterally into air filled voids within the capillary fringe. The net result of the spill is the accumulation of the bulk of the gasoline volume in a pool within the capillary fringe. A decline in the elevation of the water table can result in the spreading of gasoline further into the saturated zone. Droplets or blobs of LNAPL would then be entrapped in pore spaces at a lower elevation as the water table elevation increases.

Ethanol changes two primary properties that control the fate of gasoline in the subsurface. The partitioning of ethanol between the gasoline and the aqueous phase is significantly greater than the partitioning of petroleum hydrocarbons, leading to an increased flux of contaminants to the groundwater. The surface and interfacial tensions that cause interfacial forces, which result in the entrapment of residual gasoline in the saturated and unsaturated zones, are reduced leading to less capillary entrapment. Both of these properties change when ethanol is added to gasoline because ethanol is very hydrophilic, whereas petroleum hydrocarbon constituents are hydrophobic. The sections below provide a review of the present understanding of these two important properties.

2.3.1. Partitioning Behavior

Standard-formulation gasoline and water are almost completely immiscible. For example, Polak and Lu (1973) measured the aqueous solubilities of 21gasoline compounds. The reported values ranged between 0.54 mg/L and 1800 mg/L for 2,2,5-trimethylhexane and benzene, respectively, at 25 °C. Solubilities of water in gasoline compounds range between 74 mg/L and 690 mg/L for water in 2,3,4- trimethylpentane and benzene, respectively. The reported solubilities do not include the effects of surface-active agents or other additives to gasoline that may contain polar components in the molecular structure.

In contrast, ethanol is completely miscible in both gasoline and water at all concentrations. When ethanol is present with both gasoline and water, the preferential partitioning of ethanol into the aqueous phases modifies the overall phase behavior such that water is more soluble in gasoline, and gasoline components are more soluble in water. With a sufficiently large fraction of ethanol in the system, the gasoline and water become completely miscible with each other and merge into a single phase. Conversely, at lower ethanol concentrations, gasoline may separate into two phases if water is added to the blend.

Ethanol partitioning and the effects of ethanol on solubility are illustrated on a ternary phase diagram (Figure 2-2). Using the three axes, one can determine the overall system mass fractions of gasoline, water and ethanol for any point on the interior. The shaded region indicates the range of water, gasoline and ethanol fractions where the three components exist as two separate phases while the unshaded region indicates the composition range where these components exist as a single phase. The curve separating the two regions is called the binodal curve. On Figure 2-2 the binodal curve indicates that gasoline, ethanol and water will exist as a single phase in all relative combinations of water and gasoline provided that the ethanol present in the entire system exceeds 70 weight percent.

Tie lines transect the two-phase region and join water-rich and gasoline-rich segments of the binodal curve. These tie lines indicate the equilibrium compositions of the two phases. The points connected by the lines define the composition of the water-rich phase (on the left side of the two-phase region) and the gasoline-rich phase (on the right side of the two-phase region). The downward slope (left to right) of the tie lines indicates the preferential partitioning of ethanol into water.

The ternary phase diagram in Figure 2-2 illustrates the separation of phases following the addition of a small amount of water. The composition of a gasoline comprised of 85 percent ethanol (by volume) and 15 percent standard-formulation gasoline is indicated by point A. If water is added to this, the composition gradually changes as indicated by the arrow. Once the composition reaches that indicated by the end of the arrow, the single phase will split into two liquid phases with the compositions indicated by points A' and B'.

For smaller fractions of ethanol, as expected for RFG, much smaller quantities of water are required to cause phase separation. For instance, the American Society for Testing and Materials (ASTM) method D4806 states that if water is added at a concentration of 0.5% (by mass) to a gasoline containing 10 percent ethanol (by volume) and 14% aromatics (BTEX compounds) at 7°C (45°F), then the gasoline will separate into an alcohol-rich aqueous phase and a hydrocarbon phase.

Because gasoline is a highly complex mixture of alkane, cycloalkane, alkene and aromatic compounds, changes in the gasoline composition may affect the phase behavior. To illustrate this, ternary phase diagrams for two individual components found in gasoline— 2,2,4-trimethylpentane (an alkane) and toluene (an aromatic hydrocarbon)—are illustrated on Figure 2-3. A lower ethanol fraction would be required for phase separation if toluene were the hydrocarbon than if 2,2,4-trimethylpentane were the hydrocarbon. Additionally, the slopes of the tie lines in this figure indicate that ethanol partitions less preferentially into water from toluene than from 2,2,4-trimethylpentane. Assuming that toluene is representative of the general phase behavior of the aromatic hydrocarbons and the 2,2,4-trimethylpentane represents the properties of the alkanes, cycloalkanes and alkenes, then one could generalize that if the fraction of aromatics in the gasoline were increased the single-phase region would expand and upon phase separation, the gasoline would contain slightly more ethanol. Published phase relationships for water and ethanol in combination with a number of individual gasoline components may be found in Stephenson (1992), Letcher *et al.* (1986), and Letcher *et al.* (1992).

2.3.2. Change in Capillary Forces and Multiphase Flow Due to Presence of Ethanol

The addition of oxygenates to gasoline changes the nature of the capillary phenomena affecting gasoline infiltration and distribution at the water table due to a reduction in the interfacial and surface tensions between the phases. Figure 2-4 illustrates the extent of decrease in these values. Much of these data were collected for real gasolines equilibrated with water and ethanol (Powers and Heermann, 1999). The "C2" gasoline is a reformulated gasoline containing 5.8% ethanol by volume that was developed by Phillips Chemical Company and is certified for testing in California. Ethanol contents were varied by altering the gasoline-water volume ratio or by adding additional ethanol to the system.

The interfacial tension of the C2 system decreased in an almost perfectly linear way from 26.3 dynes/cm at 0% ethanol to 7 dynes/cm at 50% ethanol - a decrease of about 75%. In contrast, neat solvents and a surrogate gasoline comprised of xylene (20% by volume) and isooctane, had a much more significant decrease in the IFT with the addition of small volumes of ethanol (<10%) to the aqueous phase. These differences suggest that some of the other components of the C2 gasoline also strongly affect the interfacial tension and that surrogate mixtures of monoaromatics and alkanes are not representative surrogates for gasoline in studies of the gasoline migration and distribution at the water table.

The surface tension of water after equilibrating with benzene and ethanol is also presented in Figure 2-4. The surface tension drops substantially with the increase in ethanol. In contrast, the organic-air surface tensions are fairly constant with increasing ethanol concentration. The surface tension of the C2 gasoline following equilibration with water and added ethanol was 19.7 ± 0.25 over the range of ethanol contents (Powers and Heermann, 1999). Other researchers have also noted the same lack of change for the surface tensions of neat solvents in ternary (organic-ethanol-water) systems (e.g., Ross and Paterson, 1979). The independence of the gasoline-air surface tension can be explained by the near complete partitioning of the ethanol into the aqueous phase.

Due to the reduction in capillary force associated with the changes in interfacial and surface tensions, the height of the capillary fringe is reduced and depth of the gasoline pool altered. The gasoline can also enter smaller pore spaces (Demond and Roberts, 1991), potentially affecting its distribution in the vadose zone and in the gasoline pool. Ostendorf *et al*. (1993) presented a model for estimating the depth of a gasoline pool based on hydrodynamics and capillary forces. The resulting equation expresses the depth in terms of the densities of the gasoline and water, NAPL surface tension and NAPL-water interfacial tension, maximum saturation of the mobile gasoline phase, and a parameter that characterizes the pore size distribution (the "*n*" value in the capillary pressure-saturation model of van Genuchten (1980)). Assuming that this equation can also be applied to ethanol-blended gasoline, the expected trends in the depth of the gasoline pool can be evaluated. Variations in the density between the C2 gasoline that has been stripped of ethanol (ρ = 0.733 g/mL) and C2 gasoline with 10% ethanol (by volume) (ρ = 0.738 g/mL) have an insignificant effect on the calculated depth of the pool. The maximum saturation of the mobile form of the gasoline is unknown, but not expected to vary substantially. With the small variations in these properties between standard gasoline and ethanol-blended gasoline, the Ostendorf *et al*. (1993) equation is reduced to a direct dependence of gasoline pool depth on the NAPL-water interfacial tension. Thus, a reduction in the interfacial tension is expected to result

in a decrease in the thickness of the gasoline pool and a significantly larger areal extent of the gasoline pool.

Although these general trends are based on theory and experimental observations from other systems, few papers in the literature are available that specifically addressed the impacts of alcohols on multiphase flow processes pertinent during gasoline infiltration and spreading at the water table. Results of the most closely related studies previously completed are described below.

Researchers at the University of Waterloo have conducted the most extensive study addressing the impact of alcohol as an oxygenate in gasoline on the behavior of the gasoline in the subsurface (Donaldson *et al.*, 1994). The dynamics of M85 - a mixture of 85% methanol and 15% standard gasoline – infiltration and migration in both saturated and unsaturated systems was observed. The very high alcohol content of this gasoline resulted in a change from the immiscible displacement phenomena associated with standard gasolines to a miscible displacement process. Differences in density and viscosity become more important in miscible displacement processes than interfacial tension. Based on the unsaturated zone infiltration experiments, the behavior of the M-85 gasoline relative to the standard gasoline used for comparison can be characterized by:

- Less lateral spreading in the unsaturated zone.

- A decrease in the height of the capillary fringe, which resulted in the formation of the gasoline pool at a lower elevation (the depth of the capillary fringe returned to its original position after the methanol was flushed from the system).

- The formation of a gasoline pool at the water table with a smooth and regular geometry that was smaller in lateral extent.

- The formation of air bubbles in the area where the M-85 displaces water due to non-ideal mixing of the methanol and water that causes a reduction in the volume of the mixture.

- The formation of a "halo" of droplets of gasoline around the periphery of the gasoline pool and infiltration zone due to reduced methanol concentrations and reduction in the effective solubility of the gasoline constituents.

The formation of residual droplets of gasoline in the saturated zone is significant because it substantially increases the NAPL-water contact area for dissolution. In addition to the formation of these droplets by precipitation when the alcohol concentration drops, they can also be formed by multiphase displacement mechanisms as the water table elevation changes. Ryan and Dhir (1996) studied the changes in hydrocarbon entrapment at the bottom of a pool as the water table fluctuates. They found that by reducing the interfacial tension from approximately 40 to 10 dynes/cm with the addition of isopropyl alcohol, the volume of the hydrocarbon entrapped in the saturated zone was reduced from 11 to 6% of the total pore space. Thus, trends associated with the generation of these droplets are opposite depending on the mechanism involved. High alcohol concentrations tend to increase the probability of precipitation, but reduce the probability that droplets are formed during multiphase displacement.

Researchers at the University of Florida at Gainesville completed a large research project on the use of ethanol as a flushing agent to enhance the dissolution and recovery of NAPLs entrapped in the subsurface (e.g., Rao *et al.*, 1997). Although the multiphase flow characteristics

of the NAPLs were not investigated, an effort was made to understand the effects of ethanol on the capillary forces at the capillary fringe. Jawitz *et al*. (1998) conducted miscible displacement studies with ethanol-water solutions displacing pure water in a small two-dimensional sandbox that represented an unconfined aquifer. The displacing fluid was introduced through an injection well, not through the unsaturated zone. Two primary observations were made in this study: (1) the ethanol solution preferentially stayed near the top of the sand box due to its lower density than clean water; and (2) the capillary fringe was reduced in height by approximately 50%, the same percentage as the decrease in the air-water surface tension of the ethanol solution. Their studies were limited to the miscible displacement dynamics expected with neat ethanol displacing water.

One significant effect associated with a reduction in the IFT of water in the unsaturated zone is a reduction in the field capacity. Smith and Gillham (1994) noted that drainage of water from the unsaturated zone occurred with decreasing IFT, thereby increasing the rate of contaminant transport from the vadose zone to the saturated zone.

It is very difficult to predict how the effects described above would compare with the spill of an ethanol gasoline containing 10% or less ethanol by volume. If mass transfer of the ethanol to the aqueous phase is rapid relative to the rate of gasoline infiltration, it is possible that some miscible displacement dynamics could dominate the overall behavior of the infiltrating gasoline. Most of the ethanol in this case could partition into the aqueous phase, causing a change in the relative permeability of fluids in the vadose zone as the aqueous phase swells. Drainage of the ethanol-laden aqueous phase at a later time could dissolve BTEX compounds from the gasoline in a manner different than anticipated from a pool of gasohol. It is clear that changes in the retention of gasohol in the vadose zone and the size and shape of a gasoline pool at the water table would occur due to the partitioning of ethanol into the aqueous phase and resulting reduced surface and interfacial tensions and the reduced height of the capillary fringe. The extent of these effects is not known, although this would be of particular interest in defining the overall exposure and risk potential stemming from subsurface releases of oxygenated gasolines.

2.4. Research Approach

A two-dimensional sand tank was built to explore the impacts of ethanol on the migration and distribution of gasoline in the unsaturated zone. Two spill scenarios were considered—a spill of ethanol blended gasoline, or the spill of denatured ethanol after a prior spill of standard formulation gasoline. Results from the gasoline spills used for this second scenario were also used as a base case to assess the effects of ethanol in gasoline.

Experiments with denatured ethanol spills were used to evaluate potential mechanisms that could have resulted in the increase LNAPL thickness observed at the PNW site. The experiments were not, however, designed to specifically simulate this site. Significant differences in the LNAPL and porous media characteristics were required to adapt this scenario to the size of the spill tank used in this research. All of these properties were fully characterized, however, to provide qualitative comparisons.

2.4.1. Materials

2.4.1.1. Fluids

Standard 87-octane gasoline purchased from a gasoline station in Potsdam, NY was used for the 2-D spill experiments. Ethanol (Pharmco Products, Brookfield CT) was added to this gasoline to generate gasohol (10% ethanol by volume). The gasoline was dyed with a hydrophobic dye and the ethanol used in the gasohol mixture was dyed with a hydrophilic dye prior to mixing into the dyed gasoline. The dyes provided an ability to track the migration of the gasoline and the partitioning of ethanol during the infiltration process.

Characteristics of the gasoline and gasohol are presented in Table 2-1. The density of both liquids was determined by ASTM standard #D 1217-93. The gasohol density was slightly higher than that of the 87-octane gasoline. Viscosities of both were found following ASTM standard #D 445-97. The surface tension was measured using the Du Nuoy ring method (ASTM standard #D-971). The addition of ten percent ethanol had very little effect on the surface tension of the mixtures. Additional methods to characterize the interfacial properties of these fluids are described in more detail in Section 2.4.2.

A number of dyes were tested for use in the experiments. Ideally, dyes that migrate and partition in a manner similar to gasoline and ethanol were sought. A hydrophobic dye was needed for the gasoline that was highly visible, but would not dissolve into the aqueous phase. A hydrophilic dye was needed for the ethanol that would partition into the aqueous phase yet still be sufficiently soluble in gasohol. The hydrophilic dye needed to travel at the same rate as ethanol and, therefore, could not be retarded due to sorption to the quartz sand. These partitioning characteristics were very important to enable the ethanol to be tracked through the system separately from the gasoline.

Oil Red-O purchased from Aldrich Chemical Company was used as a hydrophobic dye for the gasoline at a concentration of 0.1 mg/L. Oil Blue-N (Aldrich Chemical Company) was also tested, but the contrast between the dyed gasoline and the sand was insufficient at a low saturation in the unsaturated zone. Many of the hydrophilic dyes tested, including food coloring, had a tendency to be retarded, and therefore were not representative of the actual migration of ethanol in the system. Fluorescein (Aldrich Chemical Company) seemed to better represent the actual ethanol distribution in the experiment system. This dye was added to the ethanol at 0.1 mg/L prior to blending with the gasoline.

A sample of the LNAPL from well CR-25 at the PNW site was collected and characterized for comparison to the gasolines used in the laboratory experiments. The LNAPL was more viscous than gasoline and smelled more like diesel fuel or home heating oil than gasoline. Analysis arranged and provided by T. Buscheck confirmed that the LNAPL has a bimodal distribution, comprised of a distillate with a carbon range of approximately C_7 to C_{23} and a second petroleum product with a carbon range of approximately C_{20} to C_{40} with a median at about C_{29}. The distribution of carbon ranges, as quantified by peak area in gas chromatography analysis is presented in Table 2-2. The analytical laboratory concluded that a mixture of a winter grade diesel #2 or a fuel oil #2, and a lubricating oil comprised the LNAPL at the PNW site in the vicinity of the ethanol spill.

2.4.1.2. Porous Media

Three different mixtures of medium to coarse quartz sand from U.S. Silica (Ottawa, IL) comprised the porous media for these laboratory experiments. In order to characterize the sand mixtures, the hydraulic conductivity (ASTM # D2434-68), bubbling pressure, grain densities, and grain size distribution (Figure 2-5) were measured. The porosity was determined from repeatedly packing the column (32 cm long × 2.44 cm diameter) used for measuring the hydraulic conductivity. Capillary pressure curves (Figure 2-6) were constructed using a standard Tempe cell (Soil Moisture, Santa Barbara CA) with a 0.5 bar high flow ceramic plate.

Table 2-3 summarizes the characteristics of these sands. The quartz sands #1 and #2 had similar median sizes, although the higher coefficient of uniformity for sand #1 indicates that it had a much wider range of grain sizes. Separation of the coarse and fine diameter particles in the tank was noticeable creating a non-uniform packing throughout the tank with sand # 1. The second sand mixture had a narrower grain size distribution, with a majority of the fine diameter grains eliminated (Figure 2-5). This resulted in a much more uniform sand packing. The sands had similar bubbling pressures although Sand # 1 had a higher residual saturation, as was expected for a well-graded sand. The third mixture of quartz sands was used for measurement of capillary pressure and unsaturated hydraulic conductivity properties as a function of ethanol content. All of the laboratory sands had similar median grain size as the PNW site sand.

The characteristics of the sands used in the laboratory were compared to those of sand collected from the PNW site. As can be seen from Table 2-3 and Figure 2-5, it is less uniform and finer than the media that was used in the 2-D tank. The finer grain sands cause the bubbling pressure to be much higher than in the two other mixtures (Figure 2-6). In addition the hydraulic conductivity was an order of magnitude lower than that of the two other mixtures. Although the residual saturation of water in the site sand could not be determined using the available equipment, it is expected to be much higher than the sands used for tank experiments.

2.4.2. Methods

2.4.2.1. Characterization of Fluids

Interfacial Tension Measurements. Interfacial and surface tension was measured using a du Nouy ring tensiometer purchased from Fisher Scientific. These experiments were done in order to measure interfacial tension of the LNAPLs as a function of ethanol content. The aqueous solutions contained 0–60% ethanol by volume. Procedures generally followed ASTM D971, although the two phases were allowed to equilibrate for 24 hours prior to testing.

Wettability. Because of initial observations, a bottle test was used to assess the wettability of the LNAPL from the PNW site. The experiment provides an environment for a NAPL and aqueous phase to equilibrate with a porous medium (Powers *et al*., 1996). This method is particularly useful as it allows a visual assessment of the wettability of the three-phase system without the need for specialized viewing equipment. The wettability of both quartz and PNW site sand exposed to the LNAPL from this site was assessed. Water, either distilled, deionized water (DDI) or site groundwater used in these experiments was spiked with ethanol (0–50% by volume) to determine the influence of ethanol content on wettability.

The procedure for this experiment generally involves exposing initially water-wet sand to the LNAPL to allow equilibration, followed by the addition of more water to separate and observe the distribution of fluids.

Wettability is defined by visual observation as illustrated in Figure 2-8. In a water-wet case, LNAPL does not adhere to the sand grains and can be observed to float to the top of the vial. Conversely, NAPL that coats the quartz sand indicating an oil wetting condition cannot be separated by manually disturbing the soil matrix.

Visual observations were more difficult in the experiments conducted here due to the dark nature of the PNW site sand and the low interfacial tension of the LNAPL as the ethanol content was increased. The experimental method was improved over that developed by Powers *et al.* (1996) to overcome these difficulties. The sand and LNAPL and a small amount of the water were transferred into a petri dish. Gentle stirring of the mixture allowed LNAPL that had not adhered to the sand grains to separate and float on top of the water. This LNAPL was easily observable, thereby allowing water-wet conditions to be identified.

2.4.2.2. Characterization of Multiphase Flow

It was expected that the presence of ethanol in the aqueous phase would substantially change the capillary flow characteristics of this phase in the unsaturated zone. In order to assess the significance of changes in the surface tension on the flow of the aqueous phase in the unsaturated zone, a set of multi-step out flow experiments was performed to determine both capillary pressure curves (P-S) and unsaturated hydraulic conductivity functions (k-S). Collectively, these functions are termed k-S-P functions. The apparatus and procedure used for these experiments followed that developed by Liu *et al.* (1998).

The experimental apparatus used for the multi-step outflow experiments is very similar to the standard Tempe cell used for equilibrium-based measurements of capillary pressure curves. The addition of a tensiometer and pressure transducer at the midpoint of the column allows independent determination of the piezometric head at this point. The capillary pressure within the column is adjusted by applying positive air pressure at the top of the column. Water that drains from the bottom is collected in a vial on a top-loading balance. Both the head at the tensiometer and the mass of water recovered are continuously monitored with data acquisition software. A technique developed by Ahuja and El-Swaify (1976) was used to calculate unsaturated hydraulic conductivity values from the experimental data.

The experiments were conducted with sand #3 (Table 2-3) and three aqueous solutions. The solutions were distilled deionized water (DDI), and this water with 10 and 50% ethanol added by volume. The properties of these solutions are included in Table 2-4. The column was packed once with sand #3 and all experiments repeated with the same packing to minimize differences associated with variable pore structure. The sand was flushed with substantial quantities of the fluid of interest before each new set of measurements was conducted.

2.4.2.3. Gasoline Spills in 2-D Tank

A two-dimensional stainless steel tank (1.12m × 0.68m × .003 m) with a glass front was used to simulate gasoline, denatured ethanol and gasohol spills in the unsaturated zone. Hydrophilic and hydrophobic dyes were added to the spills to track the ethanol and other gasoline

components, respectively. The glass front allowed for photographic documentation and image analysis. A schematic figure of the tank is shown in Figure 2-8. The center portion of the tank was packed with quartz sand, which is represented by the lightly shaded area. Wells, which were connected to a constant head tank, were located on each end of the tank to maintain the water level in the system. The dark shaded area in Figure 2-8 represents the wells. The wells were separated from the sand by a stainless steel screen (200 mesh size) that allows the water to enter the sand, but keeps the sand out of the wells.

The tank was packed with sand using a funnel and long hose in approximately 3-cm lifts. A water level of approximately 3 cm above the sand was maintained by continually pumping water into the tank throughout the duration of packing. Once the packing was complete, the water level was dropped in 5-cm increments and allowed to equilibrate. This process was continued until the capillary fringe reached the desired level. The top of the tank was then covered to minimize any evaporation. Using a syringe, gasoline was injected into the top of the tank at an approximate flow rate of 35 ml per minute. Figure 2-9 shows process of injecting gasoline into the tank. Pictures similar to the one shown in Figure 2-9 were taken throughout the duration of the spill to document the migration and behavior of the gasoline.

Following equilibration (approximately 24 hours), the tank containing ethanol-blended gasoline was tilted to induce flow to one of the wells and cleaned using pure ethanol. Denatured ethanol spills were scheduled following spills of gasoline. These spills were also cleaned with additional pure ethanol. In both cases, the tank was continuously flushed with water (8–10 pore volumes) to remove any residual ethanol remaining in the tank.

Table 2-5 presents the experimental conditions for each set of spills conducted. Each set of spills included a gasohol spill and then a gasoline spill followed by a spill of denatured ethanol. Red food coloring was used as a hydrophilic dye in spill set # 1 but was changed due to its high retardation in this system. The depth to the capillary fringe remained constant for all the trials but is a variable that could be changed in future experiments. Gasoline and ethanol injection rates for all experiments remained relatively constant at approximately 35 ml/min. In set #4, the volume of the spill was increased to 1.5 times the original gasoline volume to determine its significance on the behavior of the spill. The volume of ethanol spilled remained constant. The tank porosity was estimated by dividing the tank volume by the sand added to the tank. The total tank volume was known, as well as the two well volumes. The porosities achieved in the tank are slightly lower than determined in hydraulic conductivity columns (Table 2-3). The capillary fringe was determined visually as the average height prior to any gasoline entering the system. These heights were within a few centimeters of the bubbling pressure presented in Table 2-3.

2.5. Results

2.5.1. Impact of Ethanol on Capillarity

The combination of surface/interfacial tension and wettability affects the extent of capillary flow of fluids in porous media. In a water-wet system, lowered values of the aqueous phase surface tension reduce the depth of the capillary fringe, and reduced LNAPL/water interfacial tensions can reduce the entrapment and retention of LNAPL films and blobs in the unsaturated and saturated zones, respectively. When the wettability changes, significant differences in the

capillary flow occur. Under these conditions, the LNAPL can spontaneously imbibe into the porous medium—the same way that water rises in the capillary fringe.

The fact that ethanol decreases surface and interfacial tensions has previously been established (e.g., Ross and Paterson, 1979). In this work, these tensions were measured for the fluids of interest to quantify the extent of change and to compare the fluids used in the laboratory to fluids found at the PNW field site. Figure 2-10 illustrates the drop in interfacial tension (IFT) between various LNAPLs and water containing ethanol. For most of the conditions tested, the IFT of the LNAPLs in water without ethanol was on the order of 20 dynes/cm, dropping to less than 5 dynes/cm at 60% ethanol in the aqueous phase. The exception was the LNAPL from the PNW site that was equilibrated from groundwater that was also extracted from this site. In this case, the IFT with no ethanol was less than 15 dynes/cm and remained lower than other samples as the ethanol, concentration increased to ~40%. The lower IFT is probably the result of surface-active agents in the groundwater or LNAPL. These could include humic substances (Johnson and John, 1999) or extra cellular polymers produced by microorganisms (Knox and Jones, 1979; Chanmugathas and Bollag, 1988).

The surface tension (ST) of aqueous phases containing ethanol also decreased with increasing ethanol concentrations (Figure 2-11). All of the fluids behaved in the same manner, except the groundwater sample from the PNW site. The ST was lower than other samples at low ethanol concentrations. This again indicates the presence of surface-active material in this groundwater.

It was determined that ethanol has negligible impact on the ST of LNAPLs after equilibration with water and ethanol. The strong partitioning tendencies of the ethanol into the aqueous phase result in very little presence of ethanol in the LNAPL and, therefore, no change in the LNAPL ST. Data for the LNAPLs included in this work, as well as a few for comparison are shown in Figure 2-12. Ethanol also had little impact on the surface tension of gasoline when add at 10% by volume. The lower ST for the gasoline samples compared with the PNW LNAPL and toluene could result from the addition of surfactants added to gasoline as detergents to clean automobile engines during operation (Peyla, 1991).

Initial observations of the behavior of the PNW site LNAPL during IFT measurements suggested that the wetting behavior of this LNAPL in the presence of site GW and ethanol varies. A series of wettability bottle tests were completed to verify this observation. No changes were observed with any combination of sand (site sand or quartz) and concentration of ethanol when DDI water was used as the aqueous phase. Figure 2-13 illustrates results of the bottle test with site groundwater as the aqueous phase. This figure suggests that indeed the LNAPL coats quartz sand grains with increasing concentrations of ethanol in the aqueous phase. The bottle test methodology had not, however, previously been used for systems that concurrently had significant differences in interfacial tension between the bottles. Thus, additional observations were made to confirm that the changes were due to wettability rather than differences in interfacial tension. The samples were transferred to a petri dish (Figure 2-14) and the aqueous phase added to assess if the LNAPL was truly coating the sand. The bottom photo illustrates that the addition of water and mechanical stirring allowed some of the LNAPL to float away from the sand grains in the sample with 10% ethanol, but still did not allow the LNAPL to separate from sand grains for the sample with 40% ethanol, thus providing more evidence that the wettability did indeed change in this sample.

Bottle tests with the site sand behaved in the same manner as quartz sand. Figure 2-15 illustrates the results of the test after transferring the materials into a Petri dish. The lack of contrast between the dark sand and LNAPL prevented photographs from adequately illustrating the coating of LNAPL on the sand at high ethanol concentrations.

At this point, we can only speculate about the mechanisms that caused the wettability of these systems to change in the presence of ethanol. Zheng *et al*. (2001) and Zheng and Powers (2001) recently studied the mechanisms resulting in changes of wettability in systems exposed to coal tar and creosote NAPLs. They found that the high molecular weight polar components in the NAPLs could become charged at low pHs, resulting in electrostatic attraction of the NAPL to a negatively charged quartz surface. Alternatively, changes in the solvent characteristics of the NAPL could induce precipitation of these high molecular weight components. It is feasible that the presence of ethanol could change the composition of the LNAPL as some components are solubilized into the aqueous phase. The presence of a large fraction of high molecular weight components in the LNAPL at this site (>25%, Table 2-2) provides credibility to the possibility that these components contributed to the observed wettability changes. Neither of these mechanisms, nor the presence of high molecular weight components, accounts for the observed changes in wetting behavior only in systems with site groundwater. As suggested above with respect to surface and interfacial tension measurements, it is likely that this groundwater contains surfactants. It is possible that their chemical or electrostatic properties could be altered in the presence of high concentrations of ethanol, thereby altering the wetting conditions. We are not aware of any research that has investigated the mechanisms of wettability changes in these types of systems.

2.5.2. Characterization of Effects of Ethanol on Flow in the Unsaturated Zone

The presence of ethanol in the aqueous phase reduces the surface tension of that phase and the interfacial tensions between the aqueous and non-aqueous phases. In this work, the effect of variable surface tension on capillary flow characteristics was assessed through the use of multi-step outflow experiments.

Figure 2-16 illustrates the capillary pressure and unsaturated hydraulic conductivity of the aqueous phase as a function of saturation and type of fluid. As expected, the reduced surface tension results in a decrease in the capillary pressure at any given aqueous phase saturation (Figure 2-16a). This reduction will directly result in a reduction in the height of the capillary fringe when ethanol is added to water. For example, the data presented in Figure 2-16a indicate that the capillary fringe would be approximately one/half the depth with 50% ethanol in the water compared to pure water. Theoretically, the percent reduction in the bubbling pressure should be proportional to the percent decrease in the surface tensions. For the data presented here, the capillary pressure curves were not lowered quite as much as would be predicted.

Figure 2-16b illustrates that the presence of ethanol in the aqueous phase substantially reduces its hydraulic conductivity in the unsaturated zone, especially at higher saturations. Analysis of this effect shows that these differences are attributable mostly to the increase in the solution viscosity with the addition of ethanol from 0 to 50%. The increased viscosity reduces the fluid's ability to flow, which will result in slower migration of ethanol-contaminated water in the unsaturated zone relative to clean water. Only a small fraction in the reduced unsaturated

hydraulic conductivity appears to be the result of the reduced surface tension of the ethanol solutions relative to water. Additional measurements and statistical analysis will be required to better determine the underlying causes of the reduced unsaturated hydraulic conductivity.

2.5.3. Infiltration and Distribution of Ethanol-blended Gasoline

A series of spill simulations into the 2-D sand tank were completed to observe the effects of ethanol (10% by volume) in gasoline on the behavior of the gasoline during infiltration and spreading at the capillary fringe. As shown in Figures 2-10 and 2-12, the gasoline surface tension and interfacial tension were very similar between the commercial gasoline used in this set of experiments and a Phillips Certified gasoline for testing in California.

The gasoline spills behaved as expected under the conditions tested. When the gasoline entered the sand, it traveled downward until it reached the capillary fringe where it began to pool and spread outward (Figure 2-17). This pool contained a much higher saturation than seen anywhere else in the spill area. Low saturations were visible in the vadose zone in the vicinity of the spill, as was evident by the very light color of the dye. As time increased, capillary suction caused the unsaturated zone above the spill to become contaminated. A slight depression (2–3 cm) of the capillary fringe was observed in the area of the spill due to the contamination of the water by the gasoline. Gasoline in both the saturated and unsaturated zone in Sand #1 spread to a greater degree than in Sand #2 due to the small-scale heterogeneities caused by the gradation in grain sizes.

A time series of photographs for a gasohol spill compared to the gasoline spill are presented in Figure 2-17. The white area outlined shows the area of the unsaturated zone that was contamination by gasoline. The dark shaded area represents the gasoline pool and the lightly shaded area represents the area that is affected by the ethanol at the given point in time. These pictures illustrate that the presence of ethanol as an additive in gasoline had a significant impact on the infiltration of gasoline through the vadose zone. As the gasohol entered the unsaturated zone, the ethanol quickly partitioned to the residual water saturation in the vadose zone. This process occurred almost immediately as is evident in the five-minute picture. The gasoline continued to travel through the sand until it reached the capillary fringe, where it began to pool and spread laterally through the tank. The ethanol, however, was retained in the unsaturated zone, contained within the residual water. Although the saturation of the aqueous phase increased at this point which would result in drainage of the aqueous phase, the unsaturated hydraulic conductivity of this fluid would be decreased (Figure 2-16b), thereby decreasing the rate of drainage of this ethanol-laden aqueous phase.

For the conditions shown in Figure 2-17, the net impact of ethanol in gasoline is that a large majority of the gasoline reaching the capillary fringe is depleted of its ethanol content. The size, shape and apparent saturation of the gasoline pool remained unaffected by the addition of ethanol to the gasoline.

At 120 minutes and after, the apparent area of the unsaturated zone that is affected by the ethanol is larger than indicated by the fluorescein dye. This is an indication that the ethanol is actually traveling farther than the dye/visualization technique suggests. This is most likely the result of the dye being retarded, or extremely low ethanol concentrations that are not visible in the system. In the 21 hr picture this becomes more evident. A clean area surrounding the lightly shaded area can be seen, but still does not reach the capillary fringe. It appeared that this clean

region had a reduced water saturation and no residual gasoline content. Thus, the major impact of the ethanol seen in these experiments is a significant reduction in the contaminated area of the unsaturated zone. Sufficient concentrations of ethanol could exist in this area to cause a reduction in the interfacial tension of the gasoline or actually cause the gasoline to dissolve into the aqueous phase and drain downward. The reduction in the aqueous and gasoline saturations are consistent with the findings of Smith and Gillham (1994), who noted that the field capacity was reduced with decreasing surface tensions.

The experimental conditions illustrated in Figure 2-17 would most likely represent a slow leak or small volume of gasoline spilled to the subsurface. One set of spills (#4) was conducted using a larger volume of gasoline to determine the extent that ethanol is retained in the unsaturated zone under these conditions. The volume was increased to 600 ml and spilled in the same manner as previous spills. The ethanol behaved very similarly and quickly partitioned into the residual water in the vadose zone. After approximately an hour, the ethanol-ladened water began to drain into the existing gasoline pool, causing a localized area of high ethanol concentrations and increased gasoline saturation (Figure 2-18). The overall extent of the size and shape of the pool was not affected by the presence of the ethanol. The overall area with remaining residual saturations in the unsaturated zone increased from that seen in the smaller volume spills.

After comparing the final pictures of each spill, it is evident that the pool resulting from the gasoline spill has very similar characteristics as the gasohol spill. Under the conditions tested, it appears that the addition of ethanol has very little effect on the gasoline pool due to the retention of the ethanol in the unsaturated zone, except in the larger volume spill where minimal effects were seen. The main effects of ethanol were observed in the reduction of gasoline in the unsaturated zone where the ethanol appears to play a rather significant role in reducing the extent of contamination. Another important variable that may affect the observed conclusions is the depth to the capillary fringe. In the experiments conducted for this paper, the depth was kept relatively constant. If this depth were greater it is expected that more ethanol would be retained within the unsaturated zone because more residual water would be available for the ethanol to partition into. This would result in less ethanol reaching the gasoline pool at the capillary fringe. A careful analysis correlating the volume of gasohol spilled to the residual water saturation and depth to water table would be required to better understand the net retention of ethanol in the unsaturated zone.

As the ethanol-laden water drains into the existing gasoline pool, concentrations of ethanol are significantly higher than the ten percent ethanol content of the gasoline. As a result of these increased concentrations, the cosolvency effects may be significantly higher in these areas. The increased cosolvency would lead to higher concentrations of BTEX contaminants in the groundwater. These concentrations were not measured as part of this study.

2.5.4. Infiltration and Distribution of Denatured Ethanol Spills

Based on experimental observations in the 2-D tank, it was apparent that the spill of denatured ethanol into an existing gasoline pool caused much more drastic changes than the observed effects of ethanol at 10% by volume in gasohol spills. Changes in the solubility of the gasoline and the reduction in surface and interfacial tensions at the high ethanol concentrations

expected with this spill scenario both contributed to the significant impact of the ethanol spill on the distribution of gasoline in the unsaturated zone and the capillary fringe.

Figure 2-19 illustrates the infiltration of ethanol into the unsaturated zone and the net effects on the existing gasoline distribution. In this time series of pictures, the area with visible fluorescein, as depicted by the lightly shaded area in the middle of the spill area, is assumed to be the same as the ethanol contaminated area. This series of spill pictures is representative of all the experiments completed in the 2-D sand tank.

As the ethanol infiltrated through the unsaturated zone, residual gasoline was immediately mobilized and pushed ahead of the ethanol front towards the capillary fringe. Dissolving the gasoline and reducing the interfacial tension most likely caused this cleaning mechanism. The ethanol infiltrated through the unsaturated zone with a minimal amount of lateral spreading due to the low surface tension and capillary forces. Once the ethanol reached the top of the capillary fringe, it started to spread laterally to a much greater extent because its density is lower than water. Throughout this infiltration process, the gasoline was mobilized and pushed ahead of the ethanol front. A significant amount of gasoline drained from the unsaturated zone during this process.

The reduction in the surface tension of water in the capillary fringe as the ethanol reached this depth caused a second major phenomenon that controlled the overall gasoline distribution. As described above from results of capillary pressure curves (Figure 2-16a), the reduction in surface tension reduces the height of the capillary fringe. This essentially caused a local depression in the water level in the middle of the gasoline pool, into which all of the mobilized gasoline could drain and accumulate. A significant reduction (3–4 cm) in the height of the capillary fringe was evident after approximately an hour. This continued to become more evident as time progressed by increasing to an 8–10 cm drop. Even gasoline that was outside of the area immediately affected by ethanol drained into this local depression due to the gradient in the water elevation. Due to the reduced interfacial tension and, therefore, the ability for the gasoline to enter smaller pore spaces, the resulting pool of gasoline had a much higher saturation than the initial distribution of gasoline. Over time, the ethanol concentration dissipated as it diffused through the aqueous phase and the height of the capillary fringe rebounded somewhat, lifting the pool of gasoline, while still retaining some gasoline entrapped in the pore spaces at lower elevations.

In essence, the combination of solubilization and reduction in surface and interfacial tension resulted in a substantial decrease in the gasoline contamination in the unsaturated zone and the accumulation of gasoline in the saturated zone into a highly saturated pool. This pool has significantly less contact area with groundwater, which would reduce the flux of contaminants to the groundwater. The pool would also be highly mobile due to the increase in the effective permeability associated with the high saturation.

2.5.4.1. *Mechanisms that could Affect LNAPL Thickness at the PNW Site*

The spill that occurred at the PNW site in March of 1999 is similar in nature to that of the denatured ethanol spills conducted in the tank. It was known that the soil was contaminated by prior spills of petroleum products, although no known pool was evident prior to the spill of ethanol. Following the spill, a NAPL thickness was detected in several wells indicating that a pool of NAPL had formed. In addition, extremely high ethanol concentrations (> 1,000,000 ppb)

were found in the vicinity, immediately following the ethanol spill. BTEX concentrations were also found to increase in wells down gradient from the high ethanol concentrations.

The formation of a NAPL pool following the ethanol spill is likely the result of the dissolution and/or mobilization of residual contamination in the unsaturated and saturated zones at the PNW site and depression of the capillary fringe to allow accumulation of the LNAPL in a zone of high saturation. Prior to the ethanol spill, this NAPL was likely smeared throughout the saturated and unsaturated zones by the seasonal water table fluctuations. At the PNW site, a NAPL pool was not initially present, but sufficient NAPL could have existed and drained down from the unsaturated zone to form a pool at the capillary fringe. The reduced interfacial tensions resulting from the ethanol could allow an increase in the saturation of this pool. The relative permeability of LNAPL in this pool would be greatly increased, allowing flow towards and detection in monitoring wells.

Figure 2-20 illustrates the relationship between the water table elevation and LNAPL thickness in three wells at this site. The inverse relationship between water table elevation and LNAPL thickness could be attributed to the smearing of the LNAPL though the saturated zone when the water table rises. This entrapped LNAPL would have a low relative permeability, preventing its migration towards a monitoring well.

The hydraulic gradient in the immediate area of the spill is relatively small causing very slow groundwater flow. Water table fluctuations that naturally occur throughout the course of the year could cause the LNAPL pool to travel around the site. As the water table height increases and decreases the direction of the hydraulic gradient is sometimes changed in the immediate area surrounding the spill. This could result in the varying depths of LNAPL over time in some of the observation wells at the site and the observation that LNAPL thickness in one well could increase while it decreases concurrently in others.

2.6. Implications

2.6.1. Ethanol-blended Gasoline

Current mathematical models describing the fate and transport of BTEX and ethanol in groundwater from spills of gasohol assume that a pool of gasohol at the capillary fringe represents the initial condition. Experimental results presented here illustrate that the ethanol partitioning into the residual water in the unsaturated zone actually produces an initial condition that is significantly different than previously assumed. Under conditions tested to date, the retention of ethanol in the unsaturated zone actually creates an initial pool almost identical to that of a gasoline spill. The mass transfer of ethanol to the saturated zone is spread out over a long period of time due to the retention and slow drainage of ethanol from the unsaturated zone. This in effect would cause the biological electron acceptor demand in the vicinity of the source area to also be spread over a longer period of time. With the retention of ethanol in the unsaturated zone, biodegradation of ethanol will occur in this region where sufficient oxygen may be present.

Attempts to mathematically model the overall fate of ethanol and BTEX in the subsurface must incorporate the mechanisms seen in these experiments in order to more accurately depict the mechanisms that affect the initial distribution of ethanol and gasoline in the unsaturated zone. The results presented here suggest that the retention of ethanol in the unsaturated zone may be

significant. The fraction of ethanol that does partition into the aqueous phase versus that which travels with the gasoline pool depends predominantly on the volume of soil and residual water in the unsaturated zone into which the ethanol can partition. This means that the gasoline spill rate, areal extent of the spill area, residual water saturation, and depth to the capillary fringe are important variables that will affect the net impact of ethanol on the distribution of gasoline in the subsurface.

It is likely that there are some positive features of the presence of ethanol in terms of remediation efforts. The presence of ethanol in the unsaturated zone will likely stimulate the microbial community in this area, contributing to the biodegradation of ethanol and BTEX in the unsaturated zone. Pumping the gasoline during recovery efforts will also be improved with the increased LNAPL saturations in the pool area that ethanol does drain into (Figure 2-18). It is important to note, however, that the region in Figure 2-18 that contains a high concentration of ethanol could also have an increased flux of contaminants into the groundwater due to cosolvent effects.

Numerical modeling efforts that include the partitioning of ethanol into the aqueous phase of the unsaturated zone as well as the resulting change in interfacial properties, flow characteristics, and cosolvency would be required to improve our ability to predict the net impact of ethanol in gasoline on the total flux of contaminants into groundwater.

2.6.2. Ethanol Spills at Bulk Distribution Terminals

A spill of denatured ethanol at a bulk terminal with preexisting LNAPL contamination will have more significant effects than described above for spills of ethanol-blended gasoline. The ethanol will mobilize gasoline that was previously entrapped at a residual saturation in the saturated and unsaturated zone. The resulting pool of LNAPL will have a higher saturation and relative permeability, potentially causing the pool to migrate in the subsurface. However, it would now be possible to recover the pool of LNAPL through extraction wells, whereas it would have been difficult to recover it when it was distributed as a residual saturation.

Changes in the wetting characteristics associated with the PNW groundwater, LNAPL and either site or quartz sand in the presence of ethanol were unexpected. If the system does becomes LNAPL wetting, it will result in capillary flow of the LNAPL into small pore spaces. It is very difficult to recover this LNAPL—the fraction remaining in the subsurface following extraction is much higher than in a water wetting case (Hugaboom and Powers, 2001). Additional research would be required to better understand the causes of the observed reversal in the wettability of this system.

2.7. Conclusions

This research presented in this chapter found that the addition of ethanol to gasoline changes the nature of the capillary phenomena affecting gasoline infiltration and distribution at the water table due to a reduction in the interfacial and surface tensions between the phases. These changes affect the environmental behavior of gasoline containing ethanol in the following ways:

·   There is less residual gasoline entrapped in the unsaturated zone following the spill of ethanol-blended gasoline compared with a standard gasoline. The reduced surface and

interfacial tension in the presence of ethanol ultimately results in more complete drainage of fluids from the region.

- A significant fraction of ethanol partitions into the residual saturation in the unsaturated zone during gasoline infiltration. Depending on the volume of the spill, this ethanol could then drain slowly into the gasoline pool, creating a central region with high ethanol concentration. The remainder of the pool appears much the same as a spill of gasoline without ethanol.

- The fraction of ethanol retained in the unsaturated zone depends greatly on the volume of soil involved, the water content, and the rate that gasoline enters the subsurface. The rate that the ethanol-laden water in the unsaturated zone drains to the capillary fringe is limited by the increased viscosity and, therefore, reduced unsaturated hydraulic conductivity of this phase. Functional relationships to describe these processes have not yet been developed.

Bulk ethanol at bulk distribution terminals can affect the behavior of previously released fuel hydrocarbons in the following ways:

- Bulk ethanol dissolves and mobilizes LNAPL entrapped in the unsaturated and saturated zones. This process creates vadose regions with high saturation that can drain towards the capillary fringe. The net result is a substantial decrease in the LNAPL entrapped in the unsaturated zone.

- Ethanol creates a depression into which all nearby LNAPL can drain. The reduction in surface tension, and, therefore, the height of the capillary fringe in the region that ethanol infiltrates, essentially creates a depression into which all nearby LNAPL can drain. The LNAPL in this region has a reduced interfacial tension, allowing it to fill a greater fraction of the pore spaces. The net result is a region with high LNAPL saturation that would be very mobile.

- The wetting properties of the soils at the PNW site could have changed as the result of the ethanol spill. It appears that significant surfactant concentrations, which affect capillary properties, exist in the aqueous phase. It is possible that their presence could be related to the stimulation of the microbial community in the presence of ethanol. Additional research would be required to confirm these mechanisms.

2.8. Recommendations

The results of research presented in this study suggest that there is still significant uncertainty in the magnitude of the effects examined. For a ethanol-blended gasoline spill, uncertainty in the amount of ethanol that is retained in the unsaturated zone prevents us from adequately predicting the composition of gasoline that accumulates in a pool at the capillary fringe and, therefore, the flux of contaminants from the source area into groundwater. Additional research is needed at several levels to provide sufficient information to predict ethanol and BTEX fluxes to groundwater. The specific vadose zone studies that are recommended include:

- Laboratory studies to better quantify the functional relationships that control the retention of ethanol in the unsaturated zone. These studies should examine the retention of ethanol as a function of soil type, moisture content and spill rate, and should include laboratory

tests to better define the significance of the observed reversal from water wetting to LNAPL wetting.

- Numerical modeling. Improved modeling efforts are needed to better represent the complex behavior of gasoline LNAPL in the presence of ethanol. A spill of ethanol-blended gasoline into the subsurface should not be modeled as a pool of gasoline with constant composition throughout. This modeling should include the partitioning of ethanol into the aqueous phase of the unsaturated zone as well as the resulting change in interfacial properties, flow characteristics, and cosolvency.

- A field-scale test that includes the release of ethanol blended gasoline under unsaturated conditions. A field-scale controlled release is need to validate in the field processes observed in the laboratory and to calibrate predictive models of the long-term net flux of ethanol and BTEX into groundwater.

Although mostly quantitative, the results of this investigation also provide a basis for recommendations regarding the remediation of soil contaminated with ethanol or ethanol-blended gasoline:

- Increased mobility can enhance LNAPL recovery. Because the spill of ethanol into soil previously contaminated by an LNAPL consolidates the LNAPL into a pool with high mobility, an opportunity exists for effective free-phase recovery of the LNAPL that would have not have otherwise been available. Efforts to recover this LNAPL should be made in a timely fashion.

- Enhanced Bioremediation within the Unsaturated Zone. The retention of ethanol in the unsaturated zone after the spill of ethanol-blended gasoline could provide an opportunity for biodegradation of the ethanol prior to its entry into the saturated groundwater zone. Oxygen, which is likely to become limited, should be added to the unsaturated zone in some form to enhance the rate of ethanol degradation in this region.

2.9. Acknowledgements

2.10. References

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Tables

Table 2-1. Gasoline properties (± 95% confidence interval).

Property	Gasoline (87 grade)	Gasohol (10 % ethanol)
Density (g/cm^3)	0.743 ± 0.001	0.756 ± 0.001
Viscosity (cP)	3.14 ± 0.09	3.29 ± 0.01
Surface tension (dyne/cm)	22.2 ± 0.2	22.0 ± 0.1

Table 2-2. Distribution of organic molecules in the PNW site LNAPL

Carbon range	Area percent
C5-	0.02
C6-C10	7.9
C11-C14	30.5
C15-C28	36.3
C29+	25.3

Table 2-3. Porous Media properties (± 95% confidence interval)

Property	Sand #1	Sand #2	Sand #3	PNW site sand
Mean diameter (d_{50} (mm))	0.35	0.32	0.35	0.30
Coefficient of uniformity (d_{60}/d_{10})	2.47	1.33	2.02	3.59
Hydraulic conductivity (cm/sec)	0.037 ± 0.013	0.079 ± 0.003	0.044	0.0027 ± 0.0008
Bubbling pressure (cm water)	20.0	23.3	~25	34.0
Residual saturation (water)	0.07	0.04	0.03	–
Grain density (g/cm^3)	2.644 ± 0.002	2.644 ± 0.002	2.644 ± 0.002	2.655 ± 0.002
Porosity	0.376 ± 0.006	0.391 ± 0.012	0.307 ± 0.007	0.409 ± 0.006

Table 2-4. Physical properties of fluids for k-S-P measurements (22ºC).

Fluid	Density g/cm^3	Viscosity dyne s/cm^2	Surface tension mN/m
DDI	1.0064	0.01037	66.4
10% ethanol	0.9936	0.01448	42.2
50% ethanol	0.9374	0.02425	26.8

Table 2-5. Matrix of experimental conditions.

Properties	Set 1	Set 2	Set 3	Set 4
Medium used	Sand #1	Sand #2	Sand #2	Sand #2
Flow rate (ml/min)	38.0	36.0	31.0	37.5
Dyes used	Oil Blue N/Red Food coloring	Oil Red O/ Fluorescein	Oil Red O/ Fluorescein	Oil Red O/ Fluorescein
Spill volume (ml)	400	400	400	600
Depth to capillary fringe (cm)	30.6	32.5	31.0	30.7
Tank porosity	0.373	0.386	0.386	0.386
Initial capillary fringe height (cm)	19.5	20.3	20.5	20.8

Figures
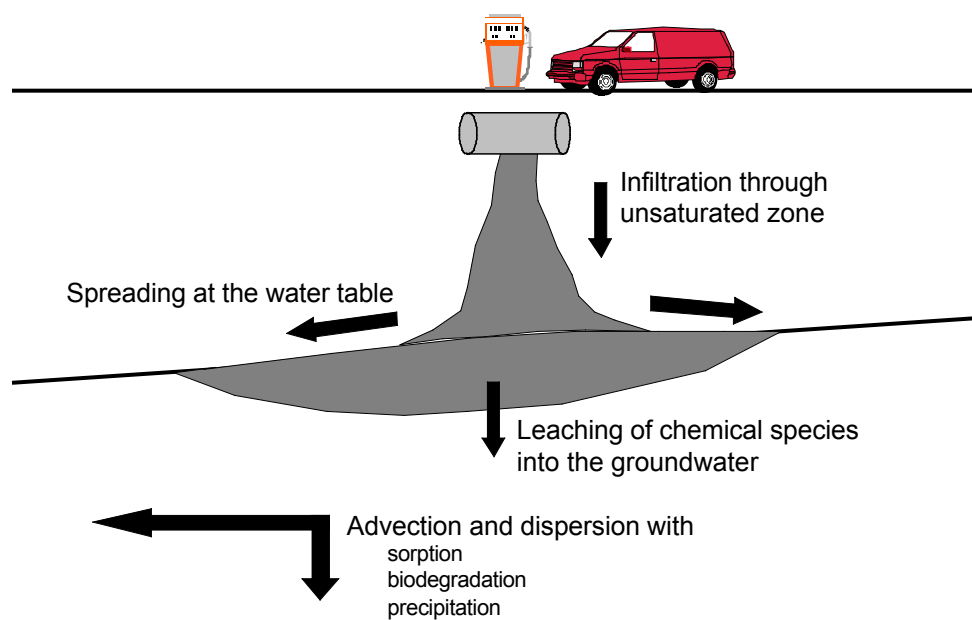
Figure 2-1. General processes governing the fate of gasoline in the subsurface.
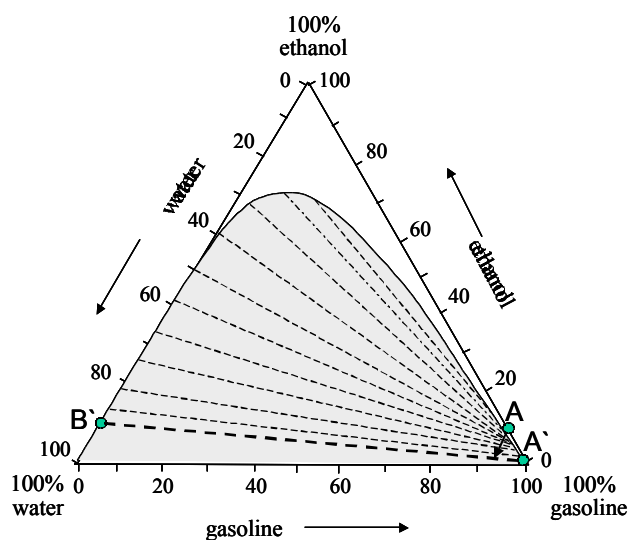
Figure 2-2. Ternary phase diagram for gasoline-ethanol-water system at 25°C adapted from de Oliveira (1997). Axes indicate percent of total mass.
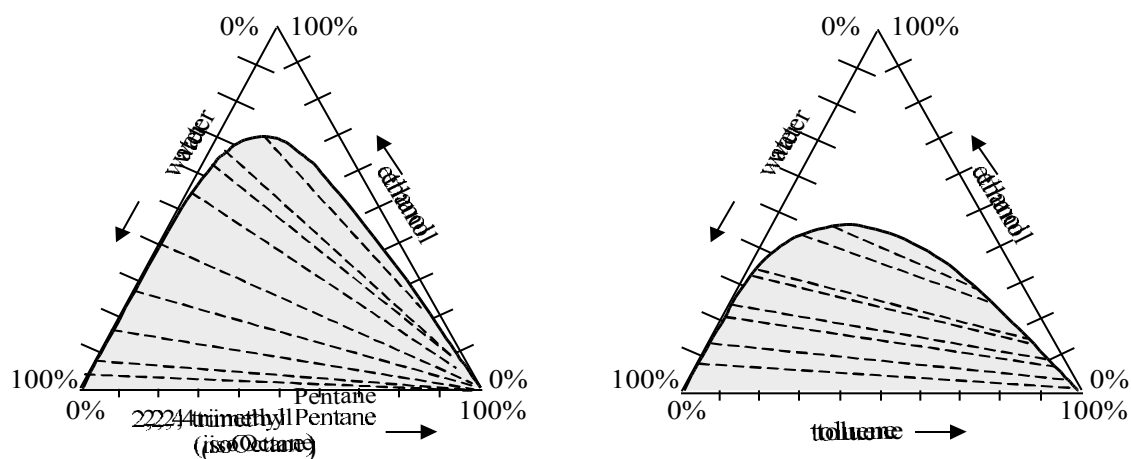
Figure 2-3. Ternary phase diagram for 2,2,4-trimethylpentane-ethanol-water system and toluene-methanol-water system at 25°C. (1995). Axes indicate mole percentages. (adapted from Peschke and Sandler, 1995).
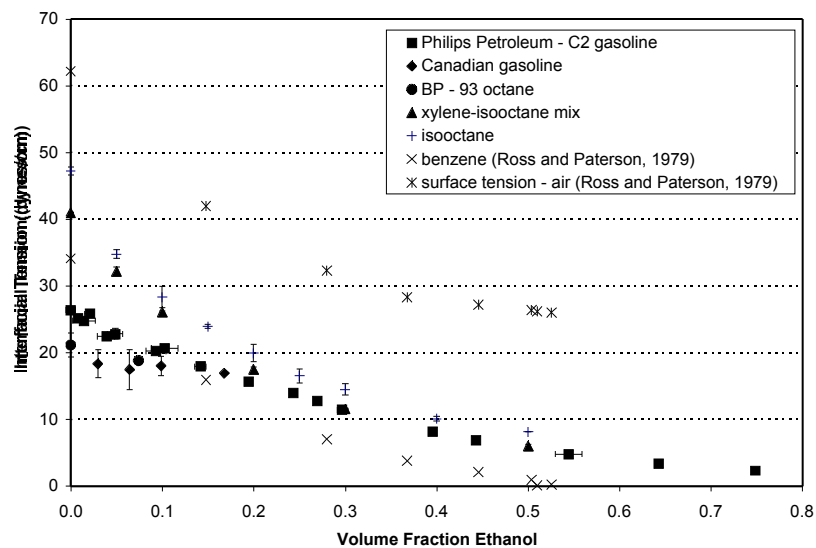
Figure 2-4. Interfacial and surface tensions of gasolines and organic chemicals in the presence of ethanol. Error bars represent one standard deviation.
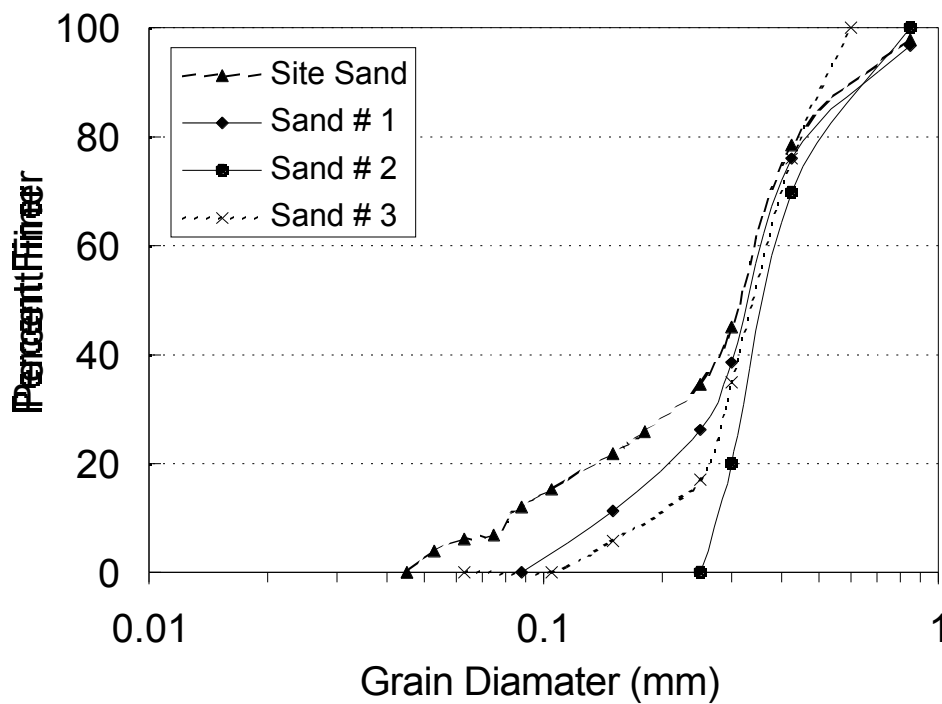
Figure 2-5. Grain size distributions for sands.
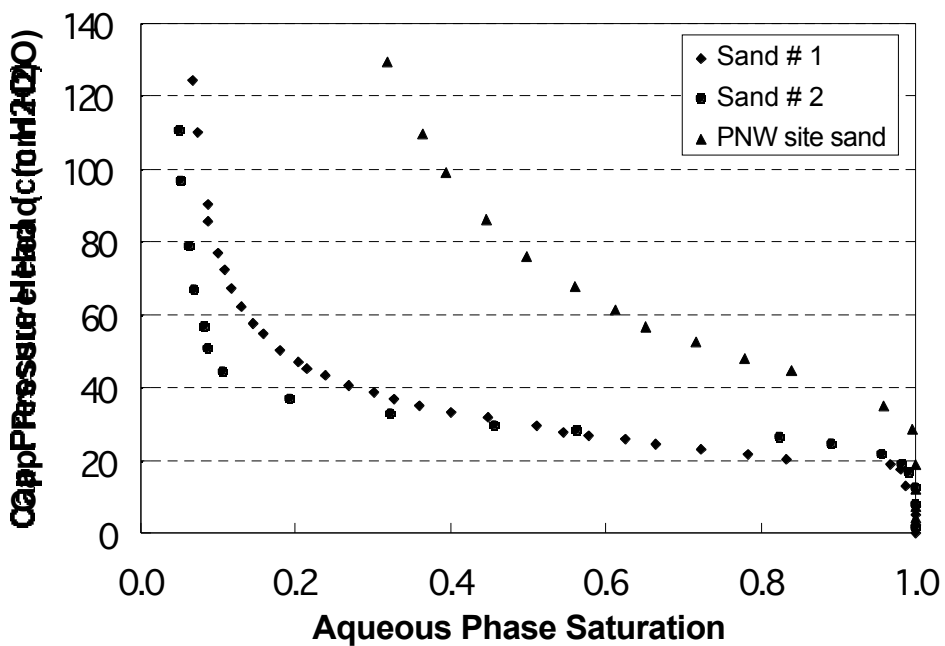
Figure 2-6. Air-water capillary pressure curves.
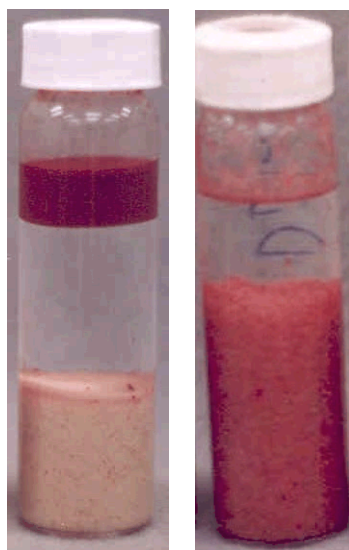
Figure 2-7. LNAPL clearly separates from the sand in the left photo indicating that the system is water wetting. In the right photo, the LNAPL coats the sand, indicating that the system is oil wetting (adapted from Powers *et al.*, 1996).
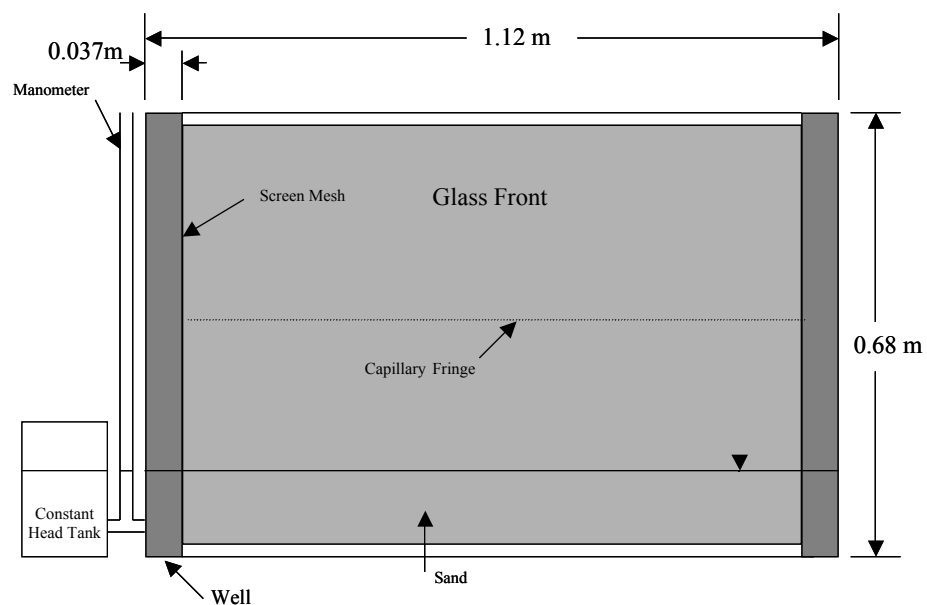
Figure 2-8. Schematic of stainless steel tank used for experiments. Dark shading represents well area and lighter shading represents the area packed with sand. Constant head tanks are located on each end of the tank. The tank is 3-cm wide.
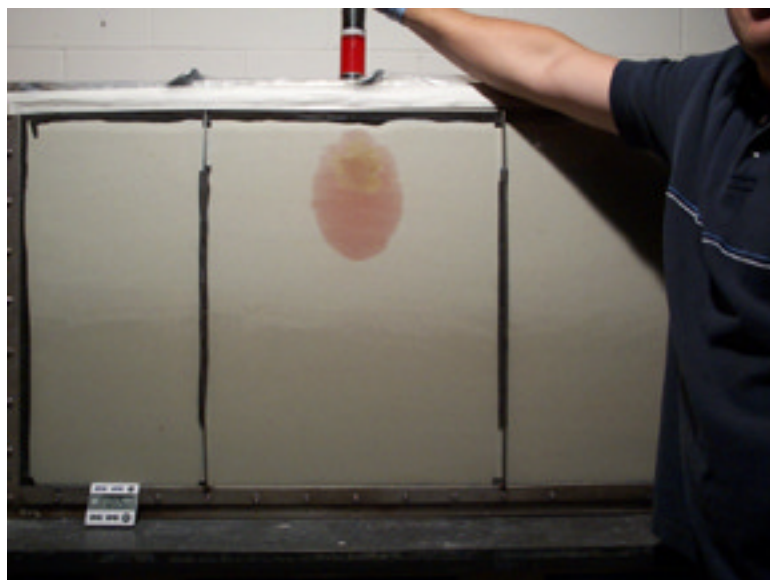
Figure 2-9. Beginning stages of a gasohol spill after 8 minutes.
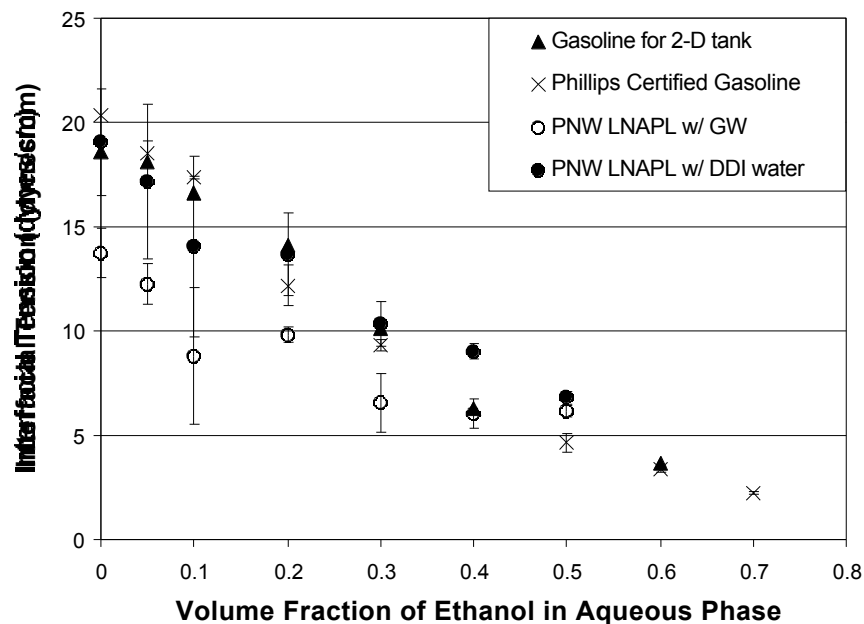
Figure 2-10. Interfacial tension of various LNAPLs. IFT measurements were made 3–5 times for each VF sample. The error bars represent one standard deviation.
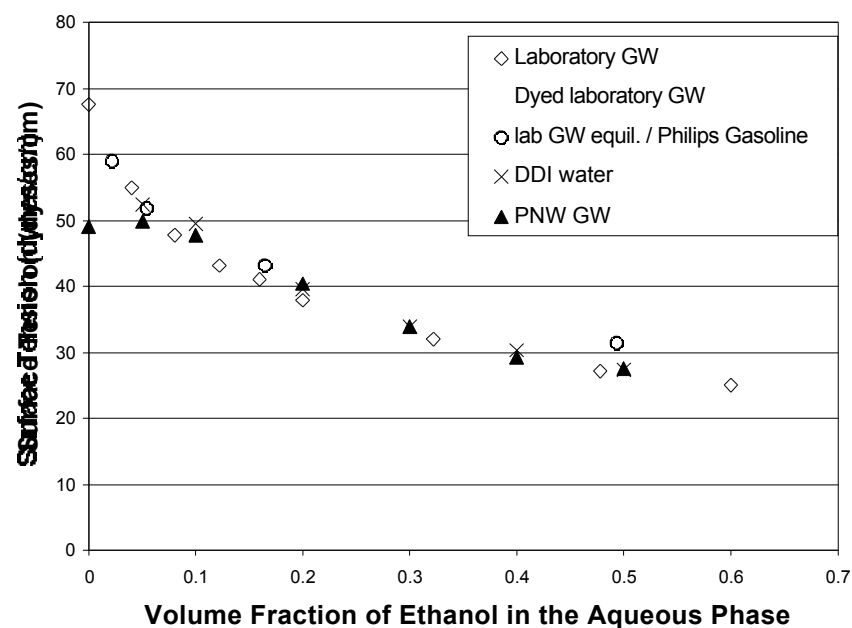
Figure 2-11. Surface tension of various aqueous phases as a function of ethanol content. Note: error bars were negligible for all measurements and are not included here.
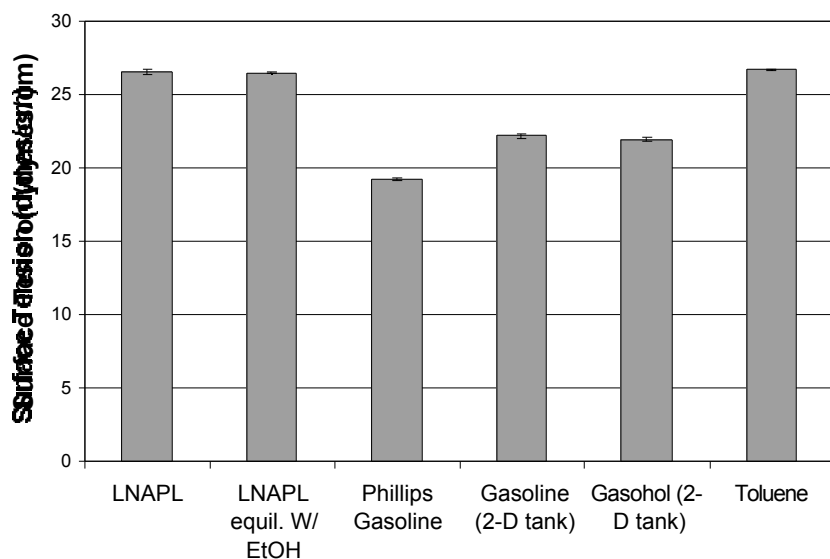
Figure 2-12. Surface tension of various LNAPLs. Error bars represent one standard deviation.
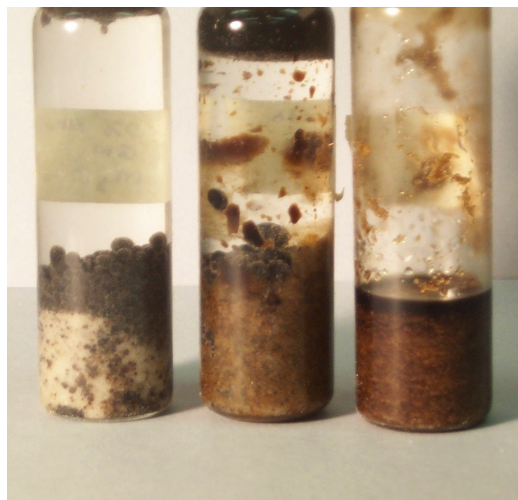
Figure 2-13. Results of the bottle test to assess wettability. Groundwater and LNAPL from the PNW site and ethanol (0, 10 and 40% by volume, L to R) were combined and equilibrated with quartz sand.

The apparent coating of LNAPL on the sand in the bottles with 10 and 40% ethanol suggest that the system changed to oil wetting in these cases.
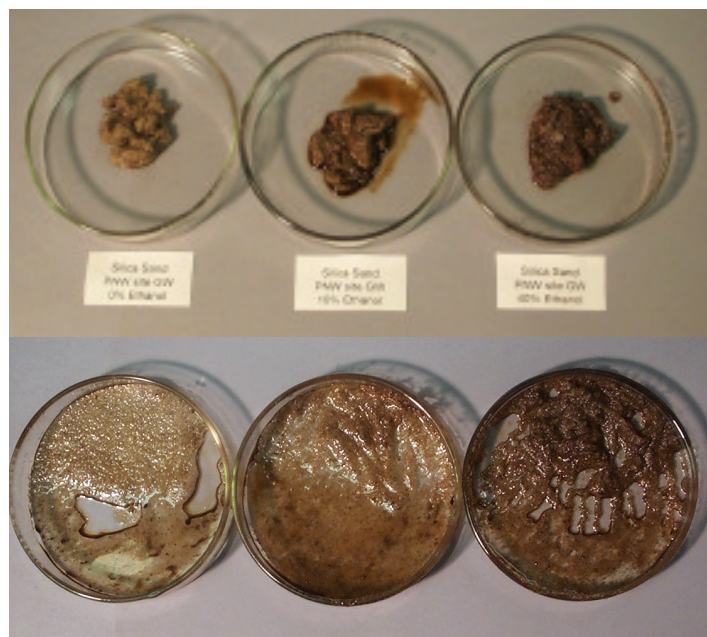
Figure 2-14. Contents from bottle tests were transferred to Petri dishes to assess if the LNAPL would separate from the sand. Both photos are quartz sand exposed to GW and LNAPL from the PNW site in the presence of ethanol (0, 10 and 40% by volume, L to R). The bottom photo was taken after the suitable aqueous phase was added to the dish.

Figure 2-15. Site sand exposed to LNAPL and GW from the site and ethanol (0, 10 and 40% by volume, L to R). The sheen associated with the samples containing 10 and 40% ethanol are associated

with the large amount of LNAPL that was retained in the sand as it was removed from the bottle. Very little LNAPL was retained in the sand from the bottle with no ethanol.
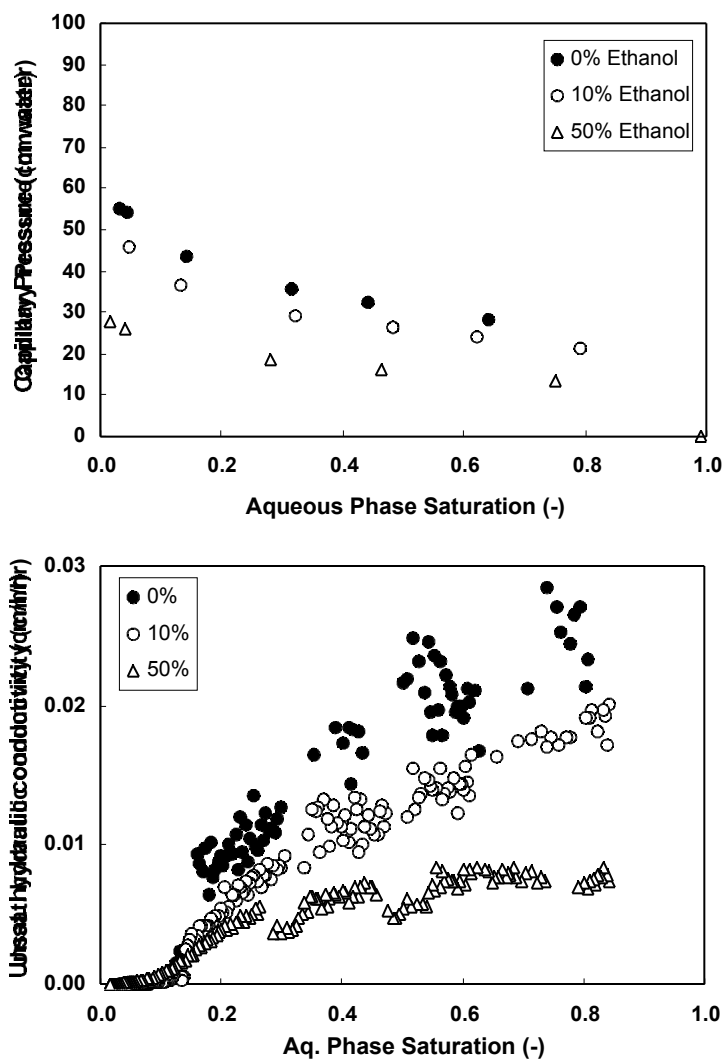

Figure 2-16. Capillary pressure (top) and unsaturated hydraulic conductivity (bottom) results from multi-step outflow experiments.
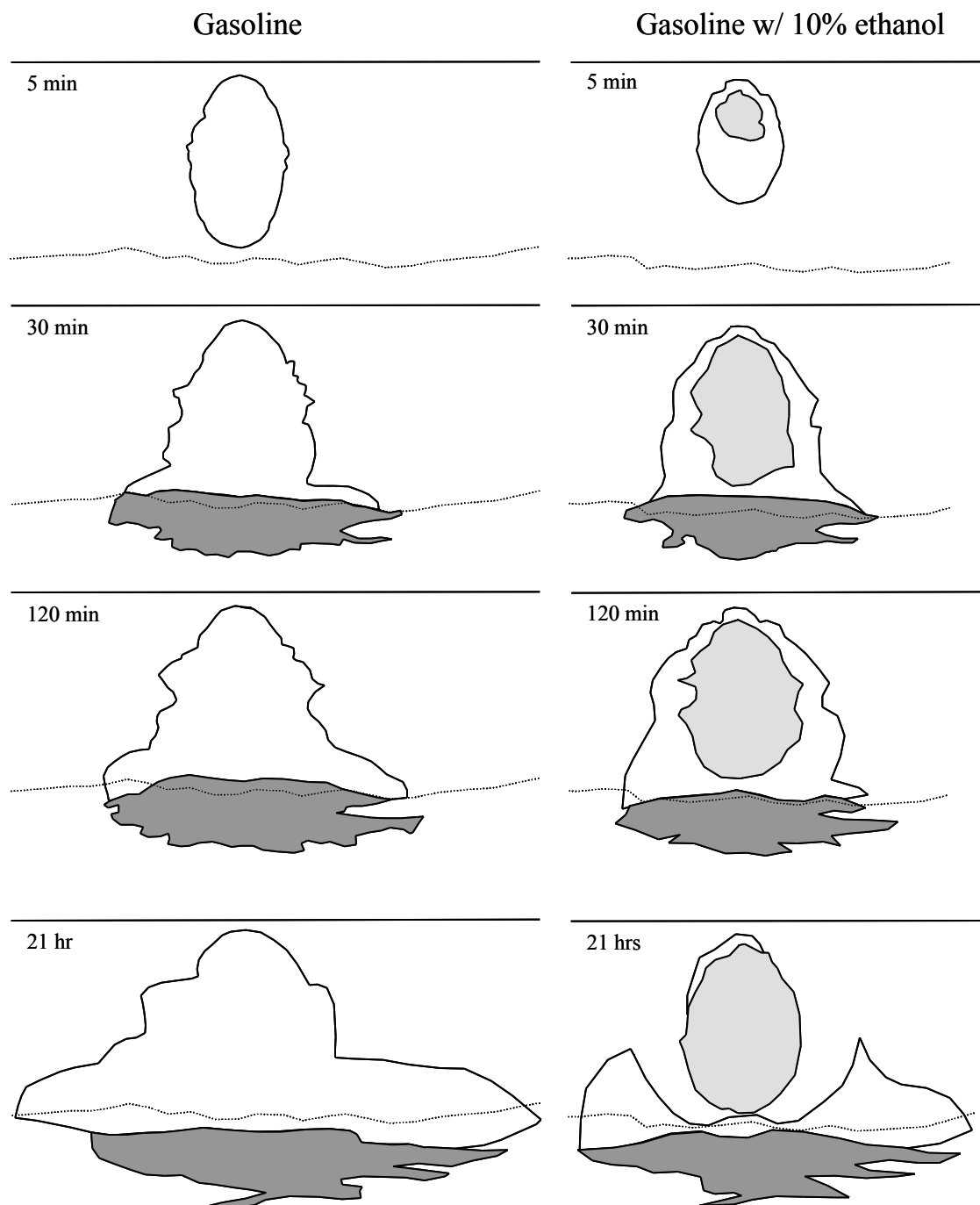
Gasoline   Gasoline w/ 10% ethanol

Figure 2-17. Time series depictions illustrating the infiltration and spreading of gasoline zone for spill 3. The left hand column represents the control case –commercial gasoline. The right hand column is the same gasoline with 10% by volume ethanol. The dashed line is the approximate location of the top of the capillary fringe as determined in the 5-minute case for each experiment. The dark shaded area represent the pool of gasoline at a high saturation, the white area represents the region within the unsaturated zone visibly contaminated by the gasoline, and the dotted region defines the area with visible concentrations of the fluorescein dye, which is considered representative of the area contaminated by ethanol.
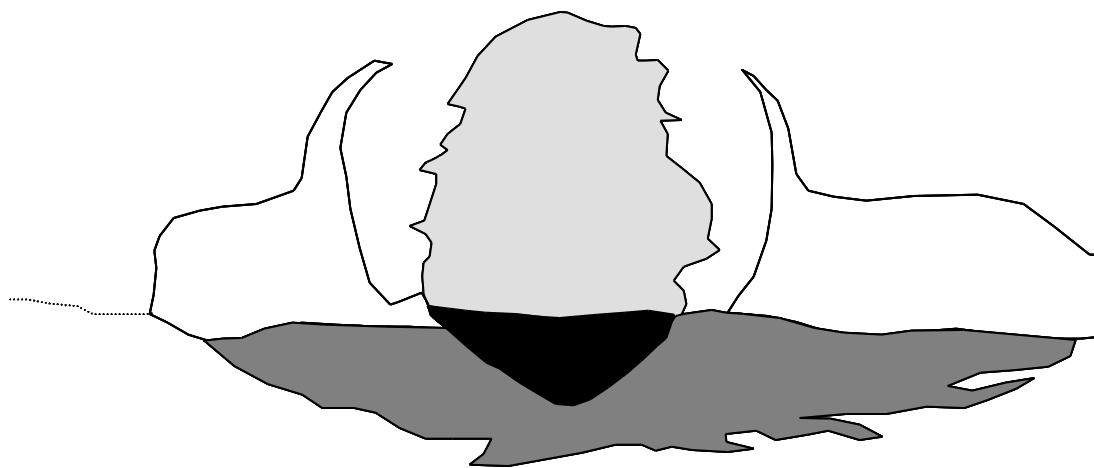
Figure 2-18. Distribution of gasoline (white and dark gray areas) and fluorescein (dotted and black areas) 20.5 hours after the beginning of a 600-mL spill of gasohol (spill 4). The black area represents the region where ethanol drained into the gasoline pool, resulting in a region of high gasoline saturation.
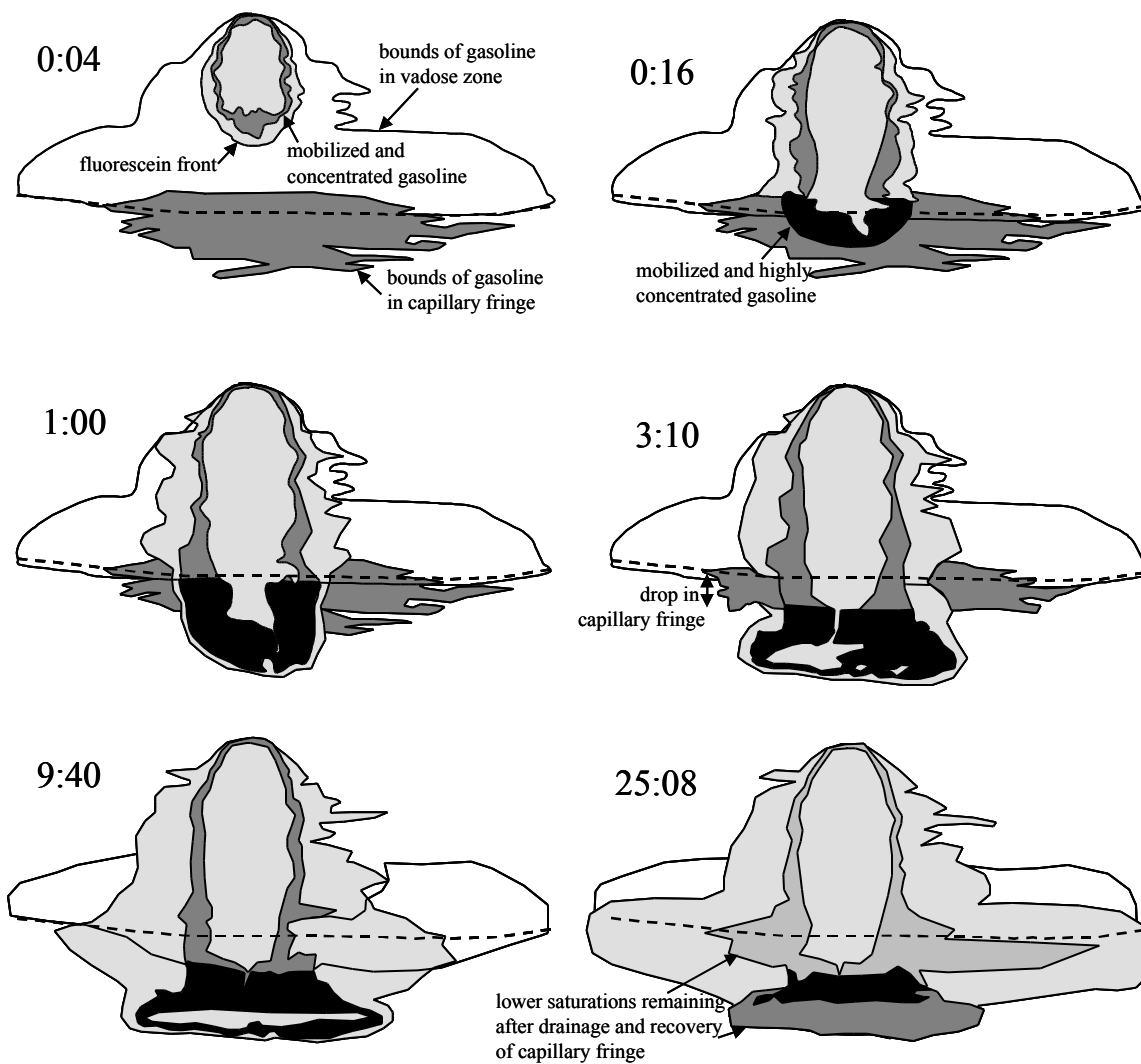
Figure 2-19. A set of pictures depicting the distribution of gasoline and fluorescein in the 2-D sand tank over time after the spill of denatured ethanol into a system with a gasoline pool and residual saturations of water remaining in the unsaturated zone.
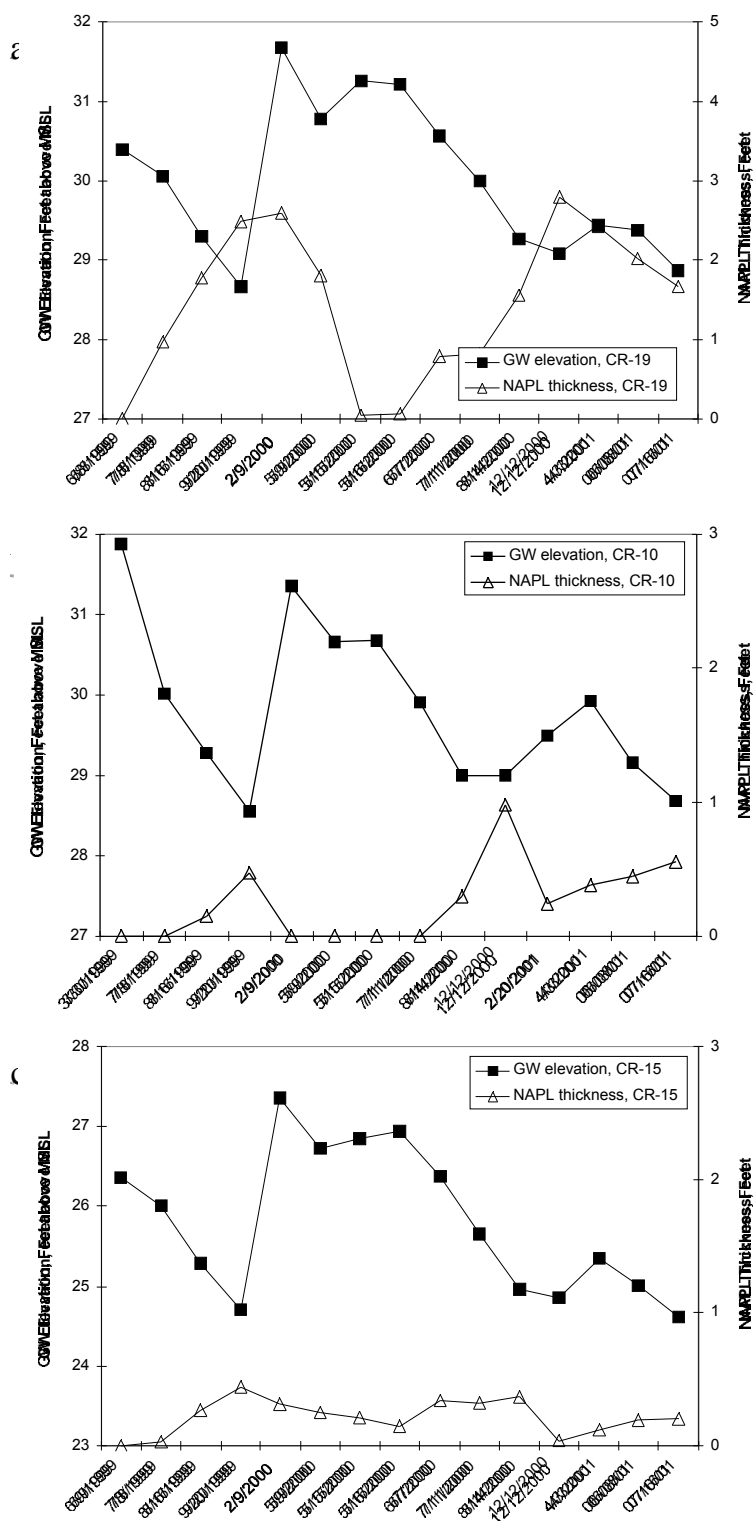
Figure 2-20. Groundwater elevation and LNAPL thickness in three wells near the ethanol spill at the PNW site.